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Reactions and Applications of Titanium Imido Complexes

NILAY HAZARI AND PHILIP MOUNTFORD*

Chemistry Research Laboratory, University of Oxford,
Mansfield Road, Oxford OX1 3TA, United Kingdom

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ABSTRACT

This Account highlights aspects of the reactions and applications of titanium imido complexes. Over the past decade in particular, the Ti=NR linkage has been shown to couple stoichiometrically with a variety of unsaturated substrates including CO₂, carbodiimides, isocyanates, isocyanides, acetonitrile, phosphalkynes, alkynes, alkenes, and allenes. Especially recently, there has been much interest in using titanium imides as catalysts for hydroamination and olefin polymerization. The advances in these areas are also reviewed.

Introduction

For over 3 decades, transition-metal complexes containing multiply bonded ligands have generated considerable interest and considerable advances have been made in understanding and developing their structures and reactivity.^{1–4} Such complexes may also play a vital role in certain industrial and biological systems. In particular, their involvement in catalysis and as reagents for synthesis has highlighted their utility.

As a terminal ligand, the formally dianionic imido (NR)²⁻ group coordinates through a metal–nitrogen multiple bond.⁵ One of the main points of interest is the reactivity of the unsaturated M=NR linkage itself. However, imido groups can also act as an ancillary or supporting ligands, as is the case for certain ring opening metathesis⁶ or Ziegler Natta⁷ olefin polymerization catalysts. Imido compounds have also been employed in the metal organic chemical vapor deposition (MOCVD) of metal nitrides.^{8,9} Furthermore, they have been implicated in the industrial ammoxidation of propylene¹⁰ and as intermediates in the enzymatic fixation of nitrogen.¹¹

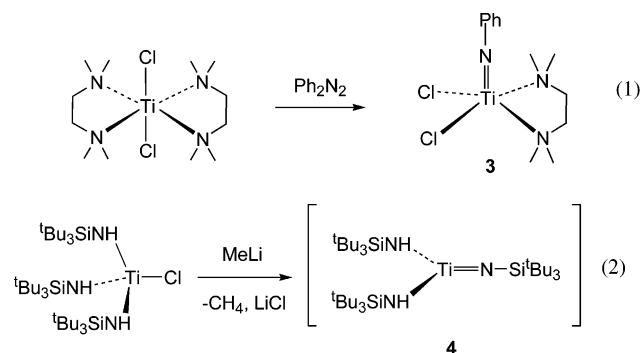
Although many examples of M=NR group reactivity are known,^{1,2} the most reactive metal–imido linkages occur in Group 4.^{2,12–14} A previous review covered aspects of titanium imido chemistry up to 1997.¹² This Account summarizes general routes to titanium imido compounds

and then focuses on recent aspects of their reactivity and applications. There is an emphasis on our own work because the space limitation of *Accounts of Chemical Research* prevents a comprehensive review. Similarly, we do not provide a detailed comparison with analogous zirconium systems.¹⁴

Preparation of Titanium Imido Complexes

The first structurally authenticated titanium imido complexes were described in 1990. Roesky et al.¹⁵ showed that reaction of TiCl₄ with (Me₃Si)₂NP(S)Ph₂ and pyridine formed **1**. Rothwell found that the η²-azobenzene ligand in Ti(η²-PhNNPh)(OAr)₂(py)₂ (Ar = 2,6-ⁱPr₂C₆H₃) was cleaved upon thermolysis, forming the phenylimido complex **2** (Figure 1).¹⁶

Besides reactions involving N–H or Si–N bond cleavage,^{2,8,12,17} titanium imido complexes can be synthesized using several other methods. Several groups have reported the preparation of imido complexes through the oxidation of Ti^{II} complexes.^{18–21} For example, TiCl₂(TMEDA)₂ reacts with Ph₂N₂, forming **3** (eq 1).¹⁸ Recently, Mindiola et al.²² demonstrated that a Ti^{IV} imido complex could be prepared from a Ti^{III} precursor through an oxidatively induced α-hydrogen abstraction reaction. Ti^{IV} imido complexes have also been prepared from TiCl₃ and TiCl₃(THF)₃.^{23,24} Another route into titanium imido complexes was through the reactions of Ti(L)Cl₂ (L = tetratolylporphyrinato²⁵ or dimethylcalix[4]arene dianion²⁶) with 2 equiv of MNHR (M = Li or K, R = alkyl or aryl). Transient imido complexes such as **4** (eq 2) can be generated from the tris(amido) species Ti(^tBu₃SiNH)₃Cl.²⁷



A useful advance toward a general route to titanium imido compounds was the report that the *tert*-butylimido complexes Ti(N^tBu)Cl₂(L)_n [L = py, *n* = 2 (**5**) or 3 (**6**); L = NC₅H₄^tBu, *n* = 2 (**7**)] could be readily obtained in multi-gram quantities from TiCl₄, ^tBuNH₂, and the appropriate pyridine (Scheme 1).^{28,29} Arylimido analogues could not be obtained directly from ArNH₂ and TiCl₄, but arylamine/*tert*-butylimide exchange reactions of **6** readily afforded arylimido complexes of the type Ti(NAr)Cl₂(py)₃ [Ar = 2,6-Me₂C₆H₃ (**8**), 2,6-ⁱPr₂C₆H₃ (**9**), Ph (**10**), Tol (**11**), or

Nilay Hazari earned a B.Sc. (honors) degree and an M.Sc. degree at the University of Sydney (1999–2003). He is currently undertaking a D.Phil. degree at the University of Oxford under the supervision of Dr. P. Mountford and Professor J. C. Green.

Philip Mountford gained a D.Phil. degree at the University of Oxford under the supervision of Professor M. L. H. Green. After a further period in Oxford as a Junior Research Fellow, he was appointed to a lectureship at the University of Nottingham. In 1998, he returned to Oxford, where he is a Reader in Inorganic Chemistry. He is a past recipient of the Royal Society of Chemistry's Sir Edward Frankland Fellowship and was recently a visiting professor at the Université Louis Pasteur, Strasbourg, and the Université Bordeaux I, France, and also at the University of Heidelberg, Germany.

* To whom correspondence should be addressed. Telephone: +44-1865-285140. Fax: +44-1865-285141. E-mail: philip.mountford@chem.ox.ac.uk.

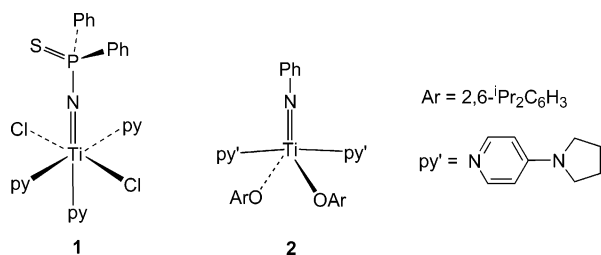
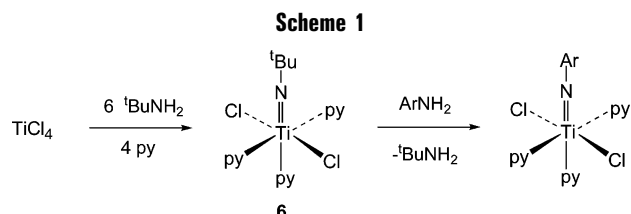


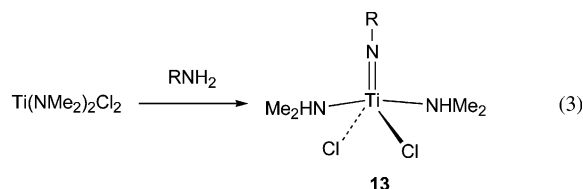
FIGURE 1. First crystallographically characterized six- (**1**)¹⁵ and five-coordinate (**2**)¹⁶ titanium imido complexes.



4-NO₂C₆H₄ (**12**).²⁹ Such exchange reactions are now a widespread method for preparing titanium arylimido complexes.³⁰ Complexes of the type Ti(NR)Cl₂(py)₃ (R = alkyl or aryl) have proven to be extremely convenient entry points into titanium imido chemistry, with a wide variety of ancillary ligands being introduced via metathesis reactions (Figure 2 shows a selection).^{12,31,32}

Another general synthetic advance was the reaction of Ti(NMe₂)₂Cl₂ with RNH₂, which provides an efficient and high-yielding route to the compounds Ti(NR)(NHMe₂)₂Cl₂ (**13**) (R = alkyl or aryl, eq 3).³³ The major advantage of this route is that it allows complexes with a wider variety of imido N substituents to be synthesized. Terminal diphenylhydrazido(2-) compounds can be prepared analogously.³⁴ Certain complexes Ti(NR)(NHMe₂)₂Cl₂ (R = alkyl, aryl, or NPh₂) have been used to prepare imido

compounds with calix[4]arene, triazacyclononane, and tris(pyrazolyl)methane coligands.^{26,34–36}



R = ^tBu, ⁱPr, CH₂Ph, Ph, 2,6-Me₂C₆H₃, 2,6-ⁱPr₂C₆H₃, 2,4,6-F₃C₆H₂, 2,3,5,6-F₄C₆H, C₆F₅, 4-ClC₆H₄, or 2,3,5,6-Cl₄C₆H

A wide range of titanium complexes incorporating a terminal imido ligand can be readily synthesized. Recent efforts have mostly focused on their reactivity. An overview of the stoichiometric and catalytic reactions and applications of titanium imido compounds follows.

Stoichiometric Reactions

C–H, H–H, and S–H Bond Activation. Several reports of C–H activation by titanium imido species have appeared. Wolczanski et al. showed that the transient species Ti(NSi^tBu₃)(NHSi^tBu₃)₂ (**4**) was capable of activating C–H bonds in benzene.²⁷ The related disiloxane transient species Ti(NSi^tBu₃)(OSi^tBu₃)₂ (**14**) was more reactive than **4**,³⁷ and these reactions have been studied computationally.³⁸ Interestingly, although **14** activated a range of alkyl (including CH₄) and aryl C–H bonds, it reacted with alkynes to form metallacycles (Scheme 2).

The reaction between Cp₂Ti(NPh) and HC≡CR (R = Ph or SiMe₃) leads to alkynyl C–H bond activation giving the anilido–acetylide complexes Cp₂Ti(NHPh)(C≡CR) (**15**).¹⁹ The reaction proceeds without observable metallacyclic intermediates. In contrast, the reaction of Cp₂Ti(NPh) with acetylene itself gives the structurally characterized azametallacycle Cp₂Ti{N(Ph)CH=CH}

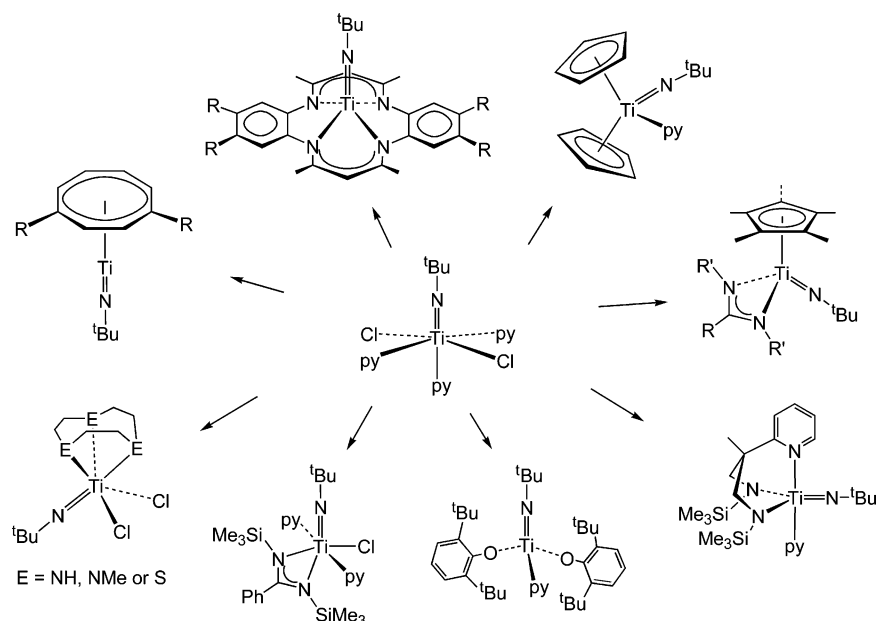
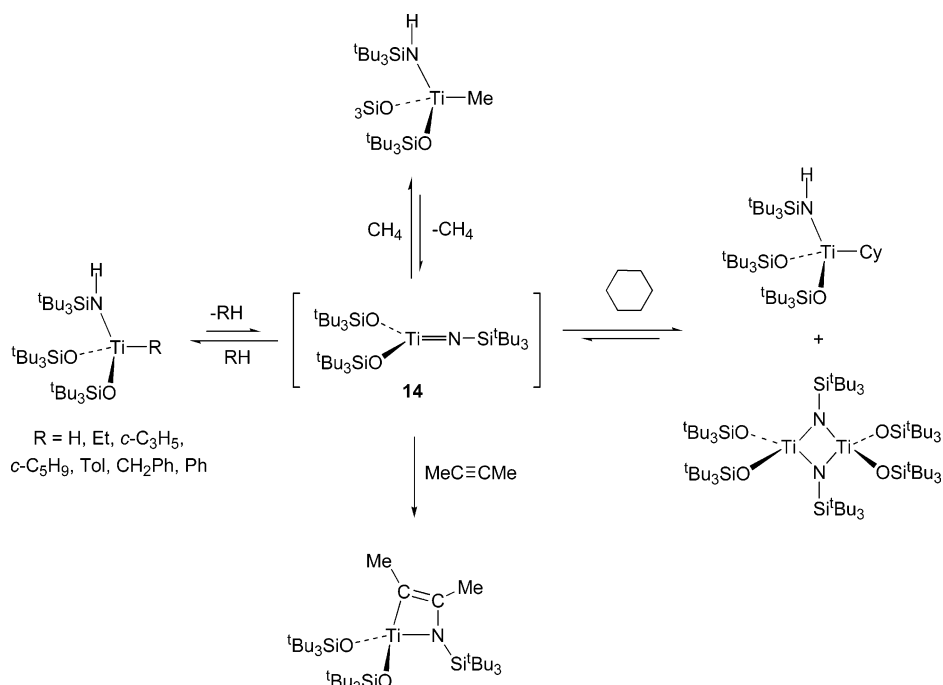


FIGURE 2. Examples of titanium imido species synthesized from Ti(N^tBu)Cl₂(py)₃ (**6**).

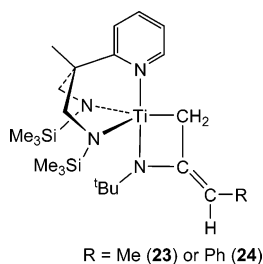
Scheme 2



(16).¹⁹ The preference for acetylenic C–H activation (deprotonation) over [2+2] cycloaddition is attributed to steric interactions between the imide and alkynyl substituents. As discussed below, activation of sp^3 -hybridized C–H bonds was observed in the reactions of $\text{Ti}(\text{N}^t\text{Bu})(\kappa^3\text{-N}_2\text{N}^{\text{py}})(\text{py})$ ($\text{N}_2\text{N}^{\text{py}} = (2\text{-C}_5\text{H}_4\text{N})\text{CMe}(\text{CH}_2\text{NSiMe}_3)_2$) (17) with $\text{MeC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or Ph),³⁹ whereas with $\text{HC}\equiv\text{CPh}$, an azametallacycle was isolated.⁴⁰

Titanium imido complexes are also capable of activating H–H and S–H bonds. For example, $\text{Cp}_2^*\text{Ti}(\text{NPh})$ ¹⁹ and homologues²¹ add H_2 in a 1,2-fashion across the $\text{Ti}=\text{NR}$ bond to form hydride–amide derivatives. $\text{Cp}_2\text{Ti}(\text{N}^t\text{Bu})(\text{py})$ (18) reacts with MeSH to yield $\text{Cp}_2\text{Ti}(\text{SMe})_2$ (19) and with H_2S to give $\text{Cp}_2\text{Ti}(\mu\text{-S})_2\text{TiCp}_2$ (20) or $\text{Cp}_2\text{Ti}(\text{SH})_2$ (21).⁴¹ The corresponding reaction of $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_4\text{taa})$ ($\text{H}_2\text{-Me}_4\text{taa} = \text{tetramethyldibenzotetraaza[14]annulene}$) with H_2S gave the terminal sulfide $\text{Ti}(\text{S})(\text{Me}_4\text{taa})$.⁴²

Reactions with Alkenes and Allenes. Wolczanski and Bennett showed that $\text{Ti}(\text{NSi}^t\text{Bu}_3)(\text{OSi}^t\text{Bu}_3)_2$ (14) reacts with ethylene to yield a mixture of the azametallacyclic product $\text{Ti}\{\text{CH}_2\text{CH}_2\text{N}(\text{Si}^t\text{Bu}_3)\}(\text{OSi}^t\text{Bu}_3)_2$ and the vinylic C–H activation product $\text{Ti}(\text{NHSi}^t\text{Bu}_3)(\text{CHCH}_2)(\text{OSi}^t\text{Bu}_3)_2$.⁴³ Andersen and Bergman have reported that $\text{Cp}_2^*\text{Ti}(\text{NPh})$ reacts reversibly with ethylene to form $\text{Cp}_2^*\text{Ti}\{\text{N}(\text{Ph})\text{CH}_2\text{CH}_2\}$ (22).¹⁹



Reaction of $\text{Ti}(\text{N}^t\text{Bu})(\kappa^3\text{-N}_2\text{N}^{\text{py}})(\text{py})$ (17) with the allenes $\text{Me}(\text{H})\text{C}=\text{C}=\text{CH}_2$ and $\text{Ph}(\text{H})\text{C}=\text{C}=\text{CH}_2$ generated corresponding titanazetidines 23 and 24, respectively.⁴⁴ The exocyclic double bonds have an *E* configuration.

Reactions with $\text{RC}\equiv\text{CR}'$, $\text{MeC}\equiv\text{N}$, $\text{RC}\equiv\text{P}$, and $\text{RN}\equiv\text{C}$.

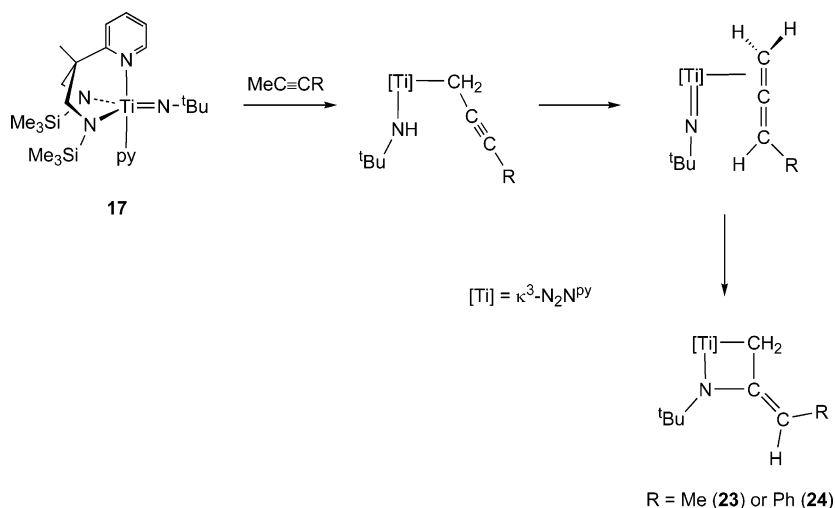
As mentioned, $\text{Cp}_2^*\text{Ti}(\text{NPh})$ reacts with acetylene to form $\text{Cp}_2^*\text{Ti}\{\text{N}(\text{Ph})\text{CH}=\text{CH}\}$ (16),¹⁹ while transient 14 (Scheme 2) also undergoes an *intermolecular* [2+2] cycloaddition reaction.⁴³ The carborane compound $\text{Ti}\{\eta^5, \eta^1\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)\text{-}(\text{C}_2\text{B}_{10}\text{H}_{10})\}(\text{N}^t\text{Bu})(\text{py})$ reacts with phenylacetylene to generate four-membered metallacycles.⁴⁵ In a series of papers, Livinghouse et al. described the use of *intramolecular* imide–alkyne cycloaddition reactions that lead to a range of organic heterocycles.^{46–48} Catalytic aspects of this work are discussed later in the section on hydroamination.

Unexpectedly, the reaction of $\text{Ti}(\text{N}^t\text{Bu})(\kappa^3\text{-N}_2\text{N}^{\text{py}})(\text{py})$ (17) with the internal alkynes $\text{MeC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or Ph) led to the titanazetidines 23 and 24 (Scheme 3),³⁹ which were also formed with $\text{Me}(\text{H})\text{C}=\text{C}=\text{CH}_2$ and $\text{Ph}(\text{H})\text{C}=\text{C}=\text{CH}_2$. It was proposed that addition of a methyl C–H bond across the $\text{Ti}=\text{NR}$ linkage occurs, followed by H atom transfer and the formation of a π -bonded allene ligand. [2+2] cycloaddition gives the titanazetidine products.

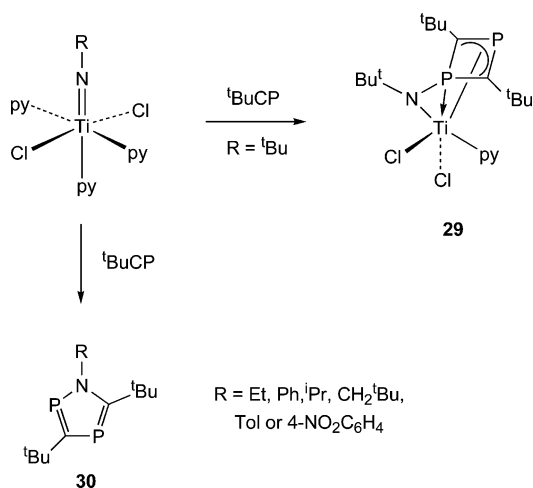
In contrast, the reaction of 17 or $\text{Ti}(\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{-}(\kappa^3\text{-N}_2\text{N}^{\text{py}})(\text{py})$ (25) with *terminal* alkynes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$ or Tol) gave the expected [2+2] cycloaddition products $\text{Ti}\{\text{N}(\text{Bu})\text{CHCR}\}(\kappa^3\text{-N}_2\text{N}^{\text{py}})$ and $\text{Ti}\{\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CHCR}\}(\kappa^3\text{-N}_2\text{N}^{\text{py}})$, respectively.⁴⁰ These reactions are discussed further in the hydroamination section.

Reactions with phosphalkynes have been described. $\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiN}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2\}(\text{py})$ (26) reacts with $^t\text{BuCP}$ to give the [2+2] cycloaddition product $\text{Ti}(\text{PC}^t\text{Bu-N}^t\text{Bu})\{\text{Me}_3\text{SiN}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2\}$ (27).⁴⁹ The phosphalkyne-derived phosphorus is bonded to the nitrogen orig-

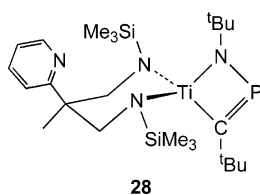
Scheme 3



Scheme 4



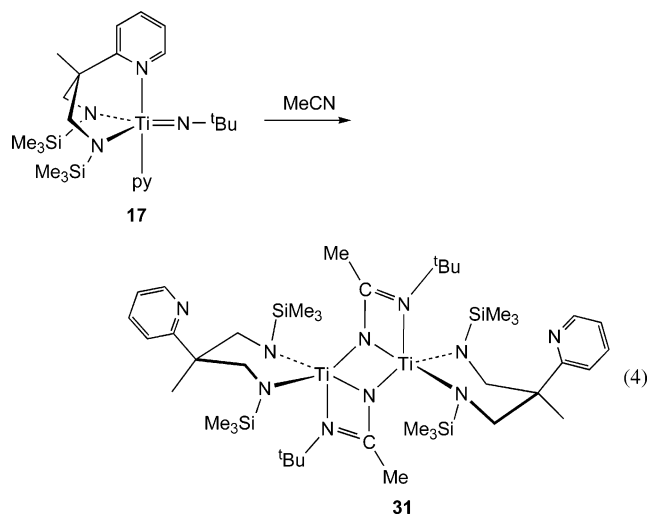
inating from the imido ligand, consistent with the respective bond polarities and steric factors. In an analogous fashion to **26**, Ti(N^tBu)(κ³-N₂N^{py})(py) (**17**) undergoes a [2+2] cycloaddition reaction with ^tBuCP to form **28**, which possesses a planar four-membered metallacycle and a κ²-bound N₂N^{py} ligand.⁵⁰



In contrast, the reaction between Ti(N^tBu)Cl₂(py)₃ (**6**) and ^tBuCP generated **29**, which contains *two* phosphorane units (Scheme 4).⁴⁹ The formation of the TiC₂P₂N core in **29** was presumed to proceed via the sequential [2+2] cycloadditions of ^tBuCP, first with Ti=NR and then with the resulting P=C bond. The course of this reaction is sensitive to the identity of the imido

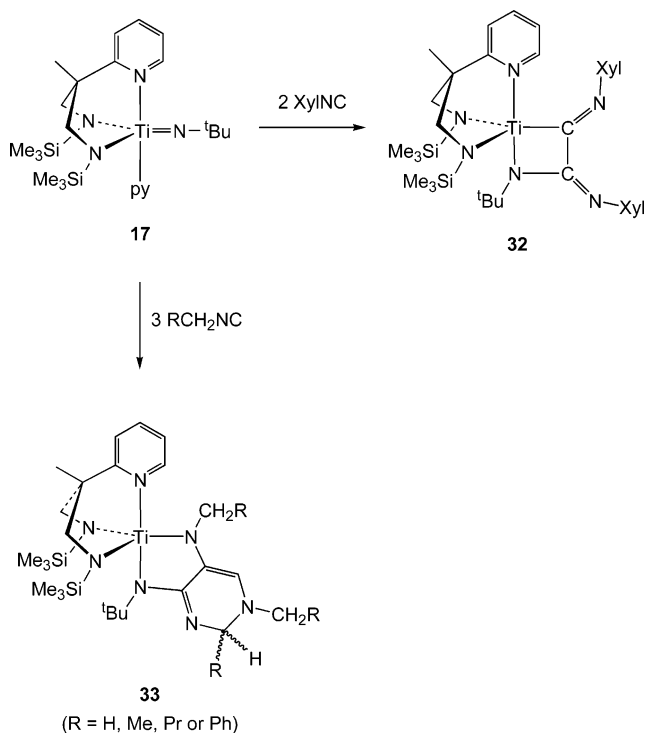
substituent. Treatment of Ti(NR)Cl₂(py)₃ (R ≠ ^tBu) with ^tBuCP gave the 1,2,4-azadiphospholes **30** (Scheme 4).⁵¹

The reaction of **17** with MeCN⁵⁰ generates the binuclear derivative **31**, which formally contains a doubly deprotonated *tert*-butylacetamidinate ligand and a κ²-bound N₂N^{py} (eq 4). The titanium centers in **31** form part of a ladder-type motif composed of three four-membered metallocyclic rings. In **31**, the carbon of the MeCN moiety is bonded to the imido-derived nitrogen, which is in contrast to that found with ^tBuCP, which favors N–P formation (cf. **28**). Compound **31** undergoes a quantitative cycloreversion reaction at elevated temperatures, yielding MeCN and four-coordinate Ti(N^tBu)(κ³-N₂N^{py}).



Treatment of **17** with the isocyanides ^tBuNC and PhNC gave no isolable products.⁵² However, the reaction with XylNC resulted in the coupling of two molecules of isocyanide with the Ti=N^tBu bond forming the titanacycle **32** (Scheme 5).⁵² No intermediates were observed. Treatment of **17** with 3 equiv of alkyl isocyanides RR'CHNC bearing a C–H bond adjacent to the NC group gave highly selective coupling with the Ti=N^tBu bond.⁵² For example, the reaction of **17** with MeNC, EtNC, ⁿBuNC, or PhCH₂NC gave the diaminodihydropyrimidine derivatives **33**

Scheme 5



(Scheme 5). These highly regioselective reactions involve both C–N and C–C bond formation as well as a C–H bond migration. A detailed mechanism was proposed.⁵²

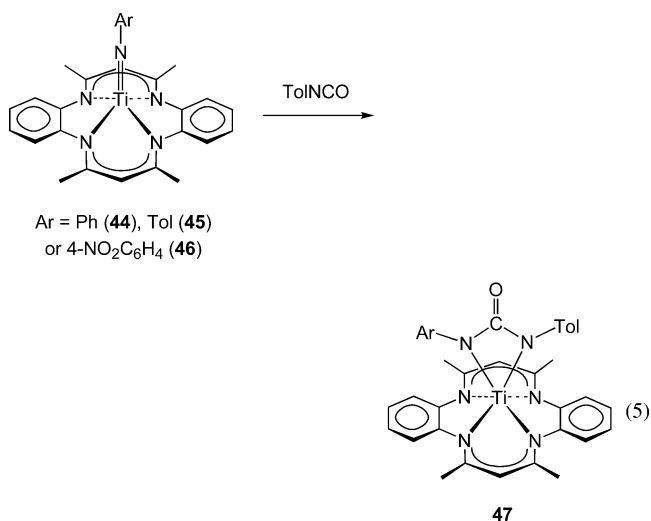
Reactions with Substrates Containing C=O or C=N Bonds. An interesting difference in reactivity was observed in reactions between the complexes $\text{Cp}^*\text{Ti}(\text{NR})\{\text{MeC}(\text{N}^i\text{Pr})_2\}$ [R = ^tBu (**34**) or 2,6-Me₂C₆H₃ (**35**)] and CO₂ (Scheme 6).⁵³ Depending upon the imido N substituent, the reaction either resulted in CO₂ cycloaddition–isocyanate extrusion or double CO₂ addition. The reaction of either **34** or **35** with CO₂ gave the N,O-bound carbamate complexes $\text{Cp}^*\text{Ti}\{\text{MeC}(\text{N}^i\text{Pr})_2\}\{\text{O}(\text{CO})\text{NR}\}$ [R = ^tBu (**36**) or 2,6-Me₂C₆H₃ (**37**)]. The *tert*-butyl derivative **36** did not react further with CO₂ but underwent a retrocyclization to yield ^tBuNCO and the μ -oxo dimer $\text{Cp}_2^*\text{Ti}_2\{\text{MeC}(\text{N}^i\text{Pr})_2\}_2(\mu\text{-O})_2$ (**38**), a reaction that has been modeled computationally.⁵⁴ Under identical conditions, the aryl derivative **37** reacted smoothly with further CO₂ to give **39**.

A marked difference in reactivity between arylimido and *tert*-butylimido compounds was also observed in the reactions between the complexes $\text{Cp}^*\text{Ti}(\text{NR})\{\text{MeC}(\text{N}^i\text{Pr})_2\}$ [R = ^tBu (**34**), 2,6-Me₂C₆H₃ (**35**), or Tol (**40**)] and isocyanates ArNCO (Ar = Tol or 2,6-Me₂C₆H₃).⁵⁵ Addition of 1 equiv of ArNCO to **35** or **40** led to the quantitative formation of N,O-bound ureates $\text{Cp}^*\text{Ti}\{\text{N}(\text{Ar})\text{C}(\text{NAr})\text{O}\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}$ (**41**). The reaction of ureate $\text{Cp}^*\text{Ti}\{\text{N}(\text{Tol})\text{C}(\text{NTol})\text{O}\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}$ with further TolNCO generated the O,O-bound biuret complex $\text{Cp}^*\text{Ti}\{\text{OC}(\text{NTol})\text{N}(\text{Tol})\text{C}(\text{NTol})\text{O}\}\{\text{MeC}(\text{N}^i\text{Pr})_2\}$ (**42**). In contrast, the reactions between $\text{Cp}^*\text{Ti}(\text{N}^i\text{Bu})\{\text{MeC}(\text{N}^i\text{Pr})_2\}$ (**34**) and isocyanates RNCO (R = ^tBu or aryl) were very slow, with ultimate products being the μ -oxo dimer **38** and the carbodiimides

^tBuNCR. NMR evidence was advanced for the N,O-bound ureate intermediates.

The macrocycle-supported complexes $\text{Ti}(\text{NR})(\text{Me}_4\text{taa})$ [R = ^tBu (**43**), Ph (**44**), Tol (**45**), or 4-NO₂C₆H₄ (**46**)] reacted with isocyanates or CO₂ to form [2+2] cycloaddition products generally of the type $\text{Ti}\{\text{N}(\text{R})\text{C}(\text{O})\text{E}\}(\text{Me}_4\text{taa})$ (E = O, N^tBu, or N-aryl).⁵⁶ For example, the reactions of **44**, **45**, and **46** with TolNCO gave the N,N-bound ureates $\text{Ti}\{\text{N}(\text{Ar})\text{C}(\text{O})\text{N}(\text{Tol})\}(\text{Me}_4\text{taa})$ (**47**) (eq 5). Treatment of $\text{Ti}\{\text{N}(\text{Ph})\text{C}(\text{O})\text{N}(\text{Tol})\}(\text{Me}_4\text{taa})$ with an excess of PhNCO gave TolNCO and $\text{Ti}\{\text{N}(\text{Ph})\text{C}(\text{O})\text{N}(\text{Tol})\}(\text{Me}_4\text{taa})$ via a slow, reversible insertion reaction into the Ti–N bond. In contrast, the reaction of **43** and ^tBuNCO gave the N,O-bound ureate $\text{Ti}\{\text{N}^i\text{Bu})\text{C}(\text{N}^i\text{Bu})\text{O}\}(\text{Me}_4\text{taa})$ (**48**).

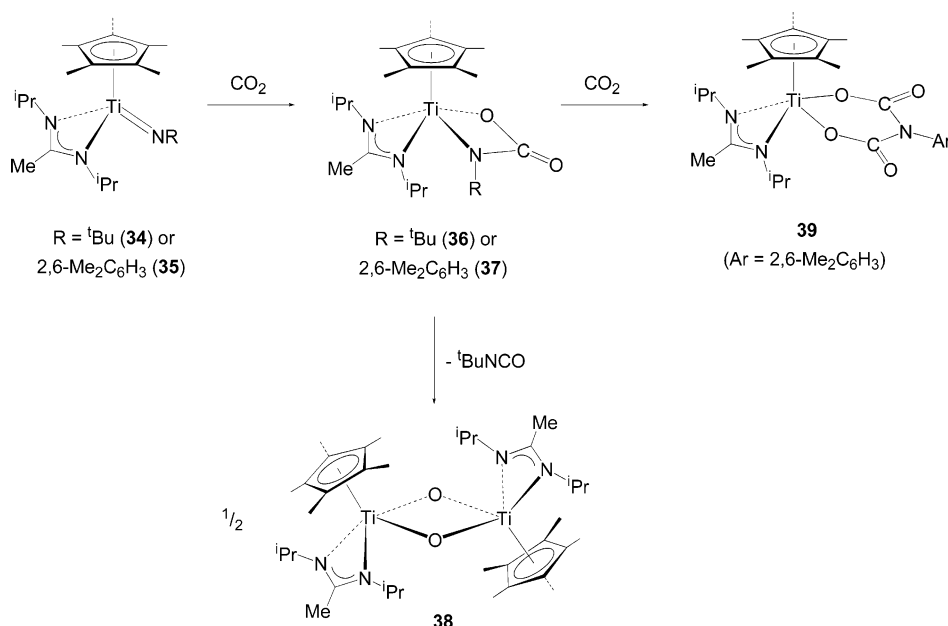
The compounds **43–46** appear to have a strong preference for forming N,N- rather than N,O-bound ureates with isocyanates. In contrast, most other Group 4 imido species form N,O-bound ureates as shown in Scheme 6 for the reactions of $\text{Cp}^*\text{Ti}(\text{NR})\{\text{MeC}(\text{N}^i\text{Pr})_2\}$ and also for the reaction of $\{\eta\text{-}1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}_2\text{Ti}(\text{NSiMe}_3)$ with Me₃SiNCO.²¹ $\text{Ti}\{\eta\text{-}5,7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}(\text{N}^i\text{Bu})(\text{py})$ reacts with PhNCO to form an oxo-titanium oligomer and PhNCN^tBu, likely via an N,O-bound ureate.⁴⁵



The reactions of the calix[4]arene-supported complex $\text{Ti}(\text{N}^i\text{Bu})(\text{Me}_2\text{calix})$ (**49**) (Me₂calix = dimethylcalix[4]arene dianion) with CO₂ and CS₂ have been reported.²⁶ The reaction of **49** with CO₂ was fast, giving $\text{Ti}\{\text{N}(\text{N}^i\text{Bu})\text{C}(\text{O})\text{O}\}(\text{Me}_2\text{calix})$ (**50**), which in turn eliminated ^tBuNCO to give $\text{Ti}_2(\text{Me}_2\text{calix})_2(\mu\text{-O})_2$ (**51**). The corresponding reaction with CS₂ was significantly slower and resulted in the formation of the bridging sulfido complex $\text{Ti}_2(\text{Me}_2\text{calix})_2(\mu\text{-S})_2$ (**52**) and ^tBuNCS without any observable intermediate of the type $\text{Ti}\{\text{N}(\text{N}^i\text{Bu})\text{C}(\text{S})\text{S}\}(\text{Me}_2\text{calix})$ (**53**). Reactions of other titanium imides with CS₂ have been reported.^{45,55}

The reactions of $\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3$ [R = ^tBu (**6**) or 2,6-ⁱPr₂C₆H₃ (**9**)] with α -diimines depend critically upon both the imido N- and diimine N- and backbone C-substituents.⁵⁷ For example, the reaction of **9** with PhNC(Me)C(Me)NPh gave the simple adduct $\text{Ti}(\text{N}\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2\{\eta^2\text{-PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}\}(\text{py})$ (**54**). In contrast, the reaction of **6** with ArNC(H)C(H)NAr (Ar = Tol or 2,6-Me₂C₆H₃) did

Scheme 6



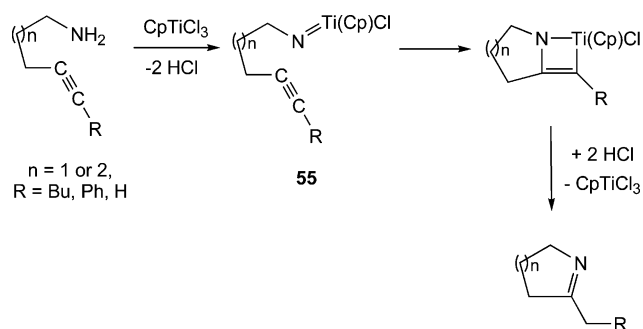
not give analogues of **54** but instead formed the corresponding $\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_3$ and $\text{}^t\text{BuNC}(\text{H})\text{C}(\text{H})\text{NAr}$. These products are those expected from a stoichiometric titanium imide/organic imine metathesis reaction. However, and in contrast to observations for zirconocene imido systems,¹⁴ while mixtures of **6** and $\text{PhC}(\text{NAr})\text{H}$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ or Tol) gave quantitative conversion to the corresponding $\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_3$ and $\text{PhC}(\text{N}^t\text{Bu})\text{H}$, kinetic studies showed that the rate-limiting step was zero-order in **1**.⁵⁸

Reactions of titanium imido compounds with PhNO , aldehydes, and ketones have all been reported^{21,45,55,59} and in each case give $\text{Ti}=\text{NR}/\text{C}=\text{O}$ or $\text{N}=\text{O}$ metathesis products. Reactions with carbodiimides have also been described,^{55,56,60,61} with the first example being for $\text{Ti}(\text{NTol})(\text{Me}_4\text{taa})$ with di-*p*-tolylcarbodiimide, which formed the corresponding biuret cycloaddition product.⁵⁶ Catalytic reactions involving carbodiimide $\text{C}=\text{N}$ bond metathesis are discussed below.

Catalytic Reactions

Hydroamination. Titanium imido complexes play a vital role in hydroamination reactions, a topical area that has been reviewed in detail recently.^{62–64} Livinghouse et al. reported the catalytic intramolecular hydroaminations of alkyl-amines using CpTiCl_3 (20% loading) to form a series of five- and six-membered cyclic imines.^{46,47} The proposed mechanism (Scheme 7) involves intermediate imido complexes of the type **55**, which undergo an intramolecular cycloaddition reaction to generate an azametallacycle, which subsequently releases the target imine regenerating CpTiCl_3 . This general methodology has also been used to prepare a range of different heterocycles using stoichiometric amounts of CpTiClMe_2 and various reagents to cleave the intermediate azametallacycles.^{46–48}

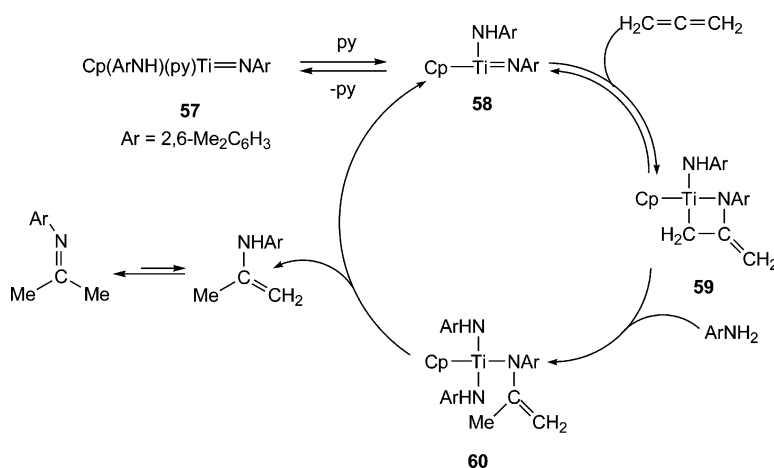
Scheme 7



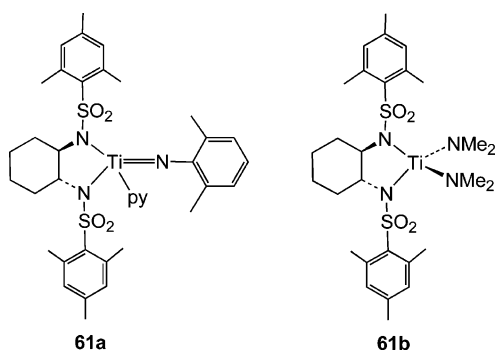
Half-sandwich titanium imido complexes have also been implicated in alkyne and allene hydroamination reactions which were initially thought to be catalyzed by the bis(cyclopentadienyl) compound Cp_2TiMe_2 (**56**). Doye reported the hydroamination of both symmetrical and unsymmetrical alkynes using **56**.⁶⁵ The regioselectivity of the reactions was of particular interest in the case of unsymmetrical alkynes because only the anti-Markovnikov product was observed. It was first suggested that **56** eliminates methane in the presence of a primary amine to generate a catalytically active titanium imido complex $\text{Cp}_2\text{Ti}(\text{NR})$. However, mechanistic studies by Bergman and Johnson suggest that the true active species is **58** (Scheme 8),⁶⁶ which arises from a cyclopentadienide/amide exchange reaction. Compound **58** can be trapped with pyridine to form **57**.

The proposed catalytic cycle for allene hydroamination is shown in Scheme 8 and proceeds via an azametallacyclobutane **59** that is rapidly protonated by amine to generate tris(amido) titanium complex **60**. This expels enamine and regenerates **58**. Density Functional Theory studies of alkyne and allene hydroamination by **58** (together with a comparison with the corresponding hypothetical reaction for alkenes) have been reported.⁶⁷

Scheme 8



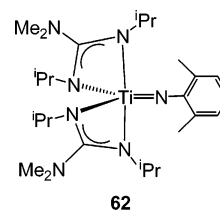
As part of a study of Group 4 bis(sulfonamido) complexes in the intramolecular hydroamination of alkynes and allenes, Bergman et al. reported that the titanium bis(sulfonamido)-supported arylimido complex **61a** catalytically converted 3-aminopropyl allene into the corresponding cyclic imine at a rate comparable to that of an analogous bis(dimethylamide) complex **61b**.⁶⁸ This supports the view that imido species are important species in the catalytic cycles for hydroamination.



Recently, the bis(guanidinate) titanium imido complex $\text{Ti}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\}_2$ (**62**) was used as a hydroamination catalyst.⁶⁹ The results of the hydroamination of four representative alkynes are summarized in Table 1. Phenylacetylene preferentially undergoes anti-Markovnikov addition with 2,6-dimethylaniline, while hydroamination of 1-hexyne generated predominantly Markovnikov products. Compound **62** was not as efficient as Bergman's $\text{CpTi}(\text{NAr})(\text{ArNH})(\text{py})$ (**57**). A number of other hydroamination systems featuring titanium imido complexes have been described and reviewed recently.^{64,70,71}

A structurally characterized imido-acetylene [2+2] cycloaddition product that corresponds to the key intermediate in the anti-Markovnikov addition of a primary amine to a terminal acetylene has been described (**63**).⁴⁰ Addition of 1 equiv of ${}^t\text{BuNH}_2$ to a solution of the related metalacyclic complex $\text{Ti}[\text{N}({}^t\text{Bu})\text{CH}=\text{CPh}]\{\kappa^3\text{-N}_2\text{N}^{\text{py}}\}$ (**64**) produced $\text{Ti}(\text{N}^i\text{Bu})(\kappa^3\text{-N}_2\text{N}^{\text{py}})(\text{py})$ (**17**) and the hydroamination

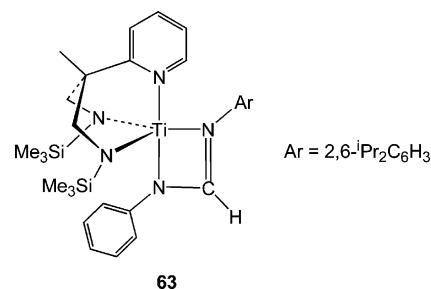
Table 1. Results for the Reaction of 2,6-Dimethylaniline with Alkynes Catalyzed by $\text{Ti}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\}_2$ (62**)**



substrate	time (h)	yield (%)	A/M ^a
PhC≡CPh	120	55	
MeC≡CMe	18	18	
PhC≡CH	18	94	73:27
C ₄ H ₉ C≡CH	48	88	14:86

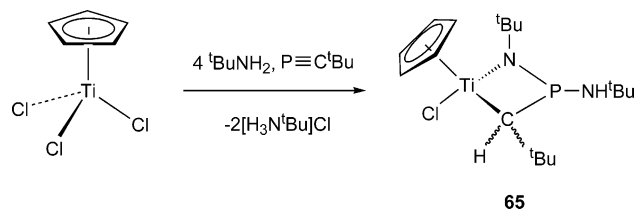
^a Ratio of anti-Markovnikov/Markovnikov products.

product *trans*-cinnamyl(*tert*-butyl)amine. Carrying out the same reaction with ${}^t\text{BuNH}_2$ and phenyl acetylene in the presence of 20 mol % of **17** at ambient temperature led to several turnovers as well as partial degradation of the Ti complex.

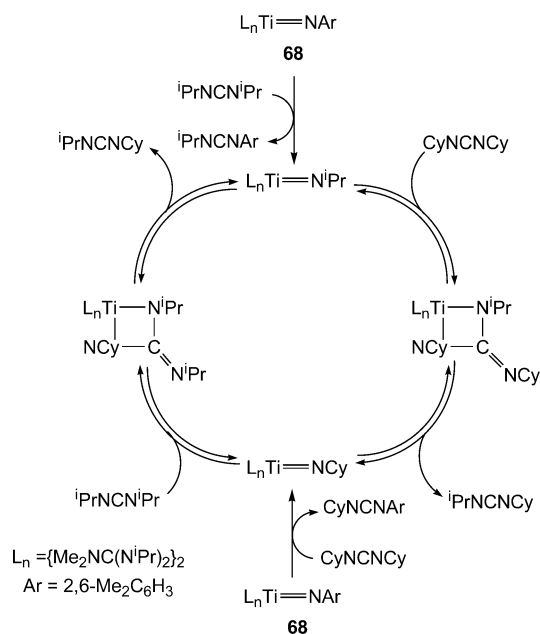


It has been suggested that titanium imido complexes may also be the active species in the hydroamination of phosphalkynes by titanium complexes. Nixon et al. showed that the reaction of catalytic amounts of TiCl_4 with RNH_2 ($\text{R} = {}^t\text{Bu}$ or ${}^i\text{Pr}$) followed by addition of ${}^t\text{BuCP}$ yields the dialkyldiaminophosphines $\text{P}(\text{NHR})_2\text{CH}^t\text{Bu}$ in near-quantitative yields.⁷² The first step in the proposed mechanism of this reaction is the formation of a titanium imido complex. More recently, Regitz and Asmus showed that the reaction of CpTiCl_3 with ${}^t\text{BuNH}_2$ and ${}^t\text{BuCP}$ yielded

Scheme 9



Scheme 10

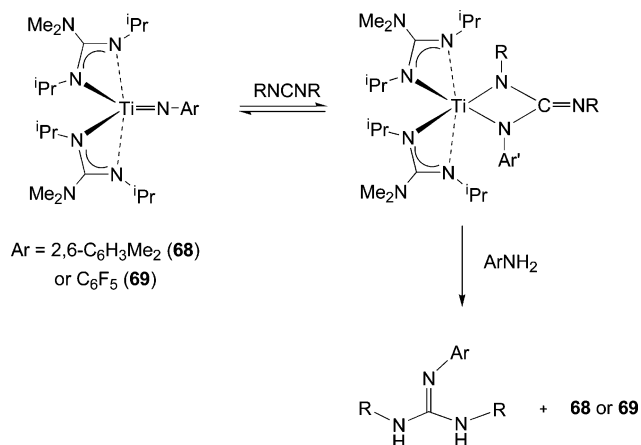


the metallocyclic complex **65** (Scheme 9), a possible intermediate in the hydroamination of phosphalkynes.⁷³

Carbodiimide Metathesis. As mentioned, $\text{Ti}(\text{NTol})(\text{Me}_4\text{taa})$ (**66**) reacts with di-*p*-tolylcarbodiimide to give $\text{Ti}\{\text{N}(\text{Tol})\text{C}(\text{NTol})\text{N}(\text{Tol})\}(\text{Me}_4\text{taa})$ (**67**).⁵⁶ This type of species has been implicated as an intermediate in carbodiimide C=N bond metathesis reactions. Richeson et al. subsequently reported that the guanidinate-supported complex $\text{Ti}(\text{NAr})\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr}_2)\}_2$ (**68**, Ar = 2,6-Me₂C₆H₃) is an effective C=N bond metathesis catalyst for alkyl- and aryl-carbodiimides.⁶¹ In the presence of a catalytic amount of **68**, metathetical exchange occurs between $i\text{PrNCN}^i\text{Pr}$ and CyNCNCy , yielding the mixed species $i\text{PrNCNCy}$ (Scheme 10). In addition to $i\text{PrNCNCy}$, other carbodiimides ArNCN^iPr and ArNCNCy were also observed. These arise from the exchange of carbodiimides with the imido ligand of **68**.

It has also been reported that the complexes $\text{Ti}(\text{NAr})\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr}_2)\}_2$ [Ar = 2,6-Me₂C₆H₃ (**68**) or C₆F₅ (**69**)] are precatalysts for the guanylation of amines with carbodiimides.⁶⁰ In the presence of either of these imides, aliphatic amines undergo direct guanylation with carbodiimides to yield trialkylguanidines in good yield. The proposed mechanism (Scheme 11) begins with [2+2] cycloaddition of a carbodiimide to the Ti=NAr bond. A proton-transfer reaction between an aromatic amine

Scheme 11

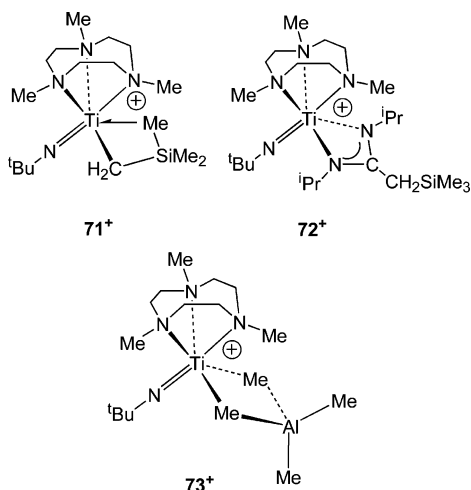


and the metal-bound dianionic guanidate ligand then releases the neutral guanidine and reforms the Ti=NR bond. The first step in this cycle was supported by the isolation of the diazametallacycle, which forms as a result of the [2+2] cycloaddition between di-*iso*-propylcarbodiimide and **69**. Complexes **68** and **69** are also capable of facilitating a transamination reaction between guanidines and amines.

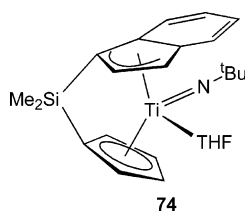
Olefin Polymerization. Initial reports of titanium imido complexes acting as ethylene polymerization catalysts appeared in 2000. A series of titanium compounds containing triazacyclononane ligands with a pendant alkylidene arm were found to be ethylene polymerization precatalysts when methylaluminoxane (MAO) was used as a cocatalyst.⁷⁴ Subsequently, Nielson et al. reported that the complexes $\text{TiCl}_2(\text{NR})(\text{TMEDA})$ (R = $t\text{Bu}$, 2- $t\text{BuC}_6\text{H}_4$, or 2- PhC_6H_4) also catalyzed the polymerization of ethylene.⁷⁵ However, even the most efficient precatalyst, $\text{TiCl}_2(\text{N}-2\text{-C}_6\text{H}_4\text{CMe}_3)(\text{TMEDA})$ had only moderate activity (ca. 13 kg(PE) mol⁻¹ h⁻¹ bar⁻¹), although it was capable of slowly polymerizing 1-hexene. The first highly active imidotitanium ethylene polymerization catalysts were only recently reported.³⁵ A family of ca. 50 precatalysts $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (R = alkyl or aryl; Me₃[9]aneN₃ = trimethyltriazacyclononane) was prepared using semi-automated procedures. High-throughput screening identified seven highly active precatalysts with activities in the range of 3400–10 000 kg(PE) mol⁻¹ h⁻¹ bar⁻¹.

Catalytically active well-defined imidotitanium mono-alkyl cations $[\text{Ti}(\text{N}^i\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{R}]^+$ [R = Me (**70**⁺) or CH₂SiMe₃ (**71**⁺)] have very recently been reported.⁷⁶ Cation **71**⁺, which has a β-Si–C⋯Ti agostic bond, reacts with di-*iso*-propylcarbodiimide exclusively at the Ti–CH₂SiMe₃ group, forming **72**⁺. Cation **70**⁺ reacts with AlMe₃ (again exclusively at the metal–alkyl bond) to form the heterobimetallic cation **73**⁺. Other macrocycle-supported cationic titanium imido complexes have been reported,⁷⁷ and very recently, Mindiola et al. reported a well-defined

cationic compound supported by a β -diketiminate ligand.²⁴



Aside from olefin polymerization, it has also been shown that the chiral *ansa*-titanocene imido complex (**74**) initiates the syndiospecific polymerization of methyl methacrylate in the presence of an aluminum activator.⁷⁸



Materials and Supramolecular Chemistry

Titanium nitride films have very useful characteristics, including excellent thermal stability and resistance to chemical attack. Winter studied a series of monomeric and polynuclear titanium imido complexes and reported that alkylimido species can be important gas-phase species in the MOCVD formation of titanium nitride films from molecular precursors.^{8,79} A number of other titanium imido compounds have been studied with regard to the MOCVD formation of TiN. For example, Carmalt and Parkin evaluated a series of complexes of the type $\text{Ti}(\text{NR})\text{Cl}_2(\text{L})_x$ ($x = 1$, $\text{L} =$ tridentate N donor; $x = 2$ or 3 , $\text{L} =$ monodentate N donor).^{9,17} Most of the precursors formed titanium nitride films. However, bulkier imido complexes and those with chelating ligands tended to produce thin films with significant oxygen and carbon contamination. The best single-source precursor was found to be $\text{TiCl}_2(\text{N}^t\text{Bu})(\text{py})_3$ (**6**), which gave gold-colored films of stoichiometry $\text{TiN}_{1.0}$. Interestingly, despite the similar nature of the coordination environment around the metal in the series of compounds examined, significant differences in film quality were observed.

Imido compounds have been minimally studied in the context of supramolecular chemistry. In the first such systematic study in Group 4, the crystal structures of a number of closely related compounds $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ (**13**) ($\text{R} =$ ^iPr , Ph, 2,3,5,6- $\text{Cl}_4\text{C}_6\text{H}_4$, 2- $\text{CF}_3\text{C}_6\text{H}_4$, 2- $^t\text{BuC}_6\text{H}_4$, or C_6F_5) were evaluated and the supramolecular interactions

were compared.³³ Except for $\text{R} = 2\text{-}^t\text{BuC}_6\text{H}_4$ and C_6F_5 , the molecules are linked in one-dimensional infinite chains by intermolecular $\text{Ti}-\text{Cl}\cdots\text{H}-\text{N}$ hydrogen bonds. For $\text{Ti}(\text{NC}_6\text{F}_5)_2\text{Cl}_2(\text{NHMe}_2)_2$, however, offset face-to-face interactions between the C_6F_5 rings led to a quite different, stacked structure. The bulky *o*- ^tBu substituent in $\text{Ti}(\text{N}-2\text{-}^t\text{BuC}_6\text{H}_4)_2\text{Cl}_2(\text{NHMe}_2)_2$ also disrupts the formation of $\text{Ti}-\text{Cl}\cdots\text{H}-\text{N}$ hydrogen-bonded chains, and this compound exists as discrete hydrogen-bonded dimers in the solid state.

Conclusion and Future Prospects

Over the last 15 years, the range of reactions involving titanium imido complexes has steadily increased. The $\text{Ti}=\text{NR}$ linkage has been shown to couple stoichiometrically with a variety of unsaturated substrates. The choice of imido N substituent is critical in these reactions and a significant difference in reactivity is often observed between alkyl- and aryl-imides. In some cases, sequential, multiple coupling reactions are facile. It has also been shown that the $\text{Ti}=\text{NR}$ moiety can activate C–H, H–H, and S–H bonds.

In addition, there are a growing number of reports describing the catalytic activity of titanium imido species, with the imido ligand either acting as a supporting ligand or reactive site. Titanium imido compounds have been used as catalysts for hydroamination, carbodiimide metathesis, and olefin polymerization. Given the enormous interest in both hydroamination and ethylene polymerization and the initial promise that titanium imido complexes have shown in performing these transformations, it is likely that research into titanium imido species will focus on these as well as other areas of catalysis in future years.

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